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THE USE OF 2,4-DINITROPHENYLHYDRAZINE TO
DETERMINE CARBONYL COMPOUNDS IN AIR
[Primenenie 2,4-dinitrofenilgidrazine dlya
opredeleniya karbonil'nykh soedineniy v vozdukh]

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THE USE OF 2,4-DINITROPHENYLHYDRAZINE TO DETERMINE CARBONYL COMPOUNDS IN AIR

I. A. Pinigina*

2,4-Dinitrophenylhydrazine (2,4-DNPH) is a selective reagent to carbonyl compounds. It readily reacts with high and low, saturated and unsaturated, aliphatic and aromatic carbonyl compounds, forming hydrazones. Therefore, 2,4-DNPH is widely used for colorimetric and chromatographic determination of various carbonyl compounds and their isomers in organic liquids and water. Until recently, 2,4-DNPH was not used to analyze air, where carbonyl compounds might be contained in microquantities.

The high reactive power of 2,4-DNPH is responsible for several difficulties when used for this purpose.

It is known that the presence of admixtures in 2,4-DNPH can reduce the hydrazone yield 50-60% (E.M. Auvinen and I.A. Faborskaya), negatively affect color stability in colorimetric determination (Basson), etc. Therefore, for analysis, the use of a reagent with a high degree of purity is recommended. The presence of excess 2,4-DNPH can also alter colorimetric and chromatographic analysis of carbonyl compounds.

In this connection, in analyzing macroquantities of carbonyl compounds, the hydrazones formed are precipitated out of the reaction mixture and then cleansed of excess 2,4-DNPH and its admixtures by double recrystallization.

In analyzing microquantities of carbonyl compounds, the hydrazones which

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have formed must not be precipitated out of the solution, i.e., they must not be cleansed of excess 2,4-DNPH and its possible admixtures. Ronkainen, subjecting these mixtures to paper chromatographic analysis, using a 50% solution of dimethylformamide in acetone as the stationary phase and hexane as the non-stationary, concluded that 2,4-DNHP itself forms 3 spots on the chromatogram with different R_f values.

Thus, microquantities of carbonyl compounds can only be analyzed in the presence of pure 2,4-DNPH, containing no admixtures, and with excess analyzing solution removed.

In our work, 2,4-DNPH was first cleansed by double recrystallization of chemically pure ethylacetate. The effectiveness of the cleansing was verified chromatographically on paper saturated with a 50% solution of dimethylformamide in ethanol. Hexane served as the stationary phase. 2,4-DNPH was recrystallized on paper in the form of 3 or more spots with various R_f values, as in the tests of Ronkainen.

The results we obtained indicated that unknown substances enter the reaction mixture, appearing on the chromatogram and, therefore, can interfere with the analysis of carbonyl compounds. To eliminate these interfering substances, all the organic liquids we used subsequently were subjected to preliminary cleansing. 0.5 ml of concentrated acid and 10 g of 2,4-DNPH hydrochloric acid were added to 1 liter of ethyl-acetate or other organic solvent; after mixing, it was left until the next day and then distilled. The twice recrystallized 2,4-DNPH in this case appears on the chromatogram in the form of 1 spot, located at the start line, i.e., it does not interfere with the determination of carbonyl compounds. However, if untreated (as described above) organic liquids are used as stationary and non-stationary phases to dissolve 2,4-DNPH, 2-3 additional spots appeared on the chromatogram with various R_f values.

However, even in the presence of pure solvents and 2,4-DNPH, excess of the latter interferes with the determination of microquantities of carbonyl compounds, as it causes the volume of the sample deposited on the chromatographic paper to be increased.

In analyzing atmospheric air, the entire sample (5-10 ml) should be used because of the low concentrations of the substances being studied. A limited amount (0.05 - 0.1 ml or less) can be taken for chromatographic analysis. Therefore, the sample must be concentrated. For this we used the characteristic of 2,4-DNPH of readily dissolving in acids and acidified water. Hydrazones which are only slightly solvent under these conditions are easily extracted by various organic solvents — isooctane, benzene, chloroform, ethylacetate, cyclohexane, carbon tetrachloride, sulfuric ether, etc. Toren and Heinrich, Zahmon, Basson, Heistand, et al. have proved that hydrazones of low-molecule aldehydes and ketones are quantitatively extracted from a water-acid hexane medium in the presence of a 1% solution of soda.

The results of our studies agree completely with the data of Lonhmon. Further chromatographic analysis showed that, along with hexane hydrazones, only a small part of 2,4-DNPH is eliminated from the acid solution, which appears on the chromatogram in the form of 1 spot at the start line and does not interfere with the analysis of microquantities of carbonyl compounds. Nearly the whole sample can thus be used for the analysis, as hexane must be evaporated, and the dry remainder is dissolved in the necessary amount of solvent and deposited on the chromatogram.

We used purified 2,4-DNPH in developing a method for separate determination of saturated aldehydes C_1-C_4 in air. For this we studied the optimal conditions for conducting a reaction between 2,4-DNPH and aldehydes, as the literature contains no clear indications about the ratio of reagents, and the effect of time and temperature on the course of the reaction.

The results, obtained in studying the reagent ratio are given in Fig. 1, where it can be seen that the effectiveness of hydrazone formation increases in proportion to the increased excess of 2,4-DNPH. The most favorable conditions for obtaining hydrazone were observed with a triple excess of 2,4-DNPH in comparison with acetaldehyde. Further increase of the reagent had no marked effect on the formation of acetaldehyde hydrazone. On the basis of these data, we recommend no less than triple excess of 2,4-DNPH to produce hydrazones.

The results of studying the effect of time on the formation of hydrazones are given in Fig. 2, where it can be seen that by the 2nd hour the reaction had basically ended. Further increase of time has no marked effect on the formation of acetaldehyde hydrazone. Therefore, we recommend producing acetaldehyde hydrazone in 3 hours in the presence of not less than a triple excess of 2,4-DNPH.

Hydrazones were produced at room temperature, as 2,4-DNPH is unstable when heated; at 60°, it already begins to dissolve.

We also used the optimal conditions for producing acetaldehyde hydrazone (triple excess of 2,4-DNPH and 3-hour exposure) to produce hydrazones of formaldehyde, propionic and butyryl aldehydes. Analogous results were attained which enabled us to recommend them also for producing hydrazones of these aldehydes.

For paper chromatographic separation of low-aldehydes C_1-C_4 , better results were recorded with the use of a 50% solution of dimethylformamide in ethanol as the stationary phase and hexane as the nonstationary phase. The time of chromatographic separation was 3-4 hours.

Separation lasts 15-20 minutes in the thin silica gel layer; however, formaldehyde and acetaldehyde do not completely separate. Better results are obtained with the use of a mixture of hexane, ethyl-acetate and chloroform in a 7:3:5 ratio as the non-stationary phase.

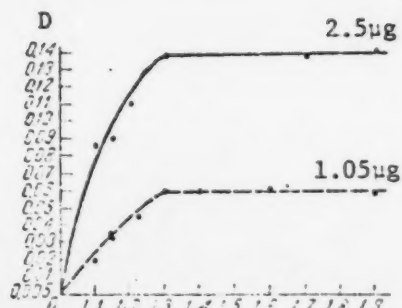


Figure 1. The effect of excess 2,4-DNPH on the effectiveness of hydrazone formation.

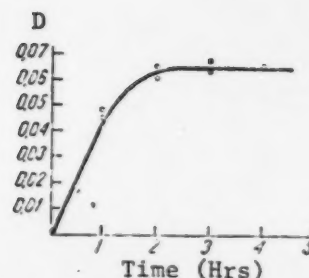


Figure 2. The effect of time on the effectiveness of hydrazone formation.

It is recommended that a quantitative determination of aldehydes after chromatographic separation be conducted as follows. The yellow spots formed by the hydrazones, are cut out of the chromatogram and transferred to a test tube with 2 ml of acetone — to elute the dye. In 10-15 minutes, 0.5 ml of 20% solution of alkali is added to the eluate. The red color with maximum absorption of 440-450 mμ which has formed is stable for more than 2 hours.

The amount of aldehydes in the sample was quantitatively evaluated with the use of a graph, plotted in advance for hydrazones of each of the aldehydes.

In determining aldehydes C_1-C_4 in air, as our research showed, samples must be taken by aspiration through 3 serially-connected absorbers with a porous plate. Each instrument is filled with 5 ml of a 0.001 M solution of 2,4-DNPH in 2 n. solution of hydrochloric acid. The absorbing instruments are cooled with a water-ice mixture. The aspiration rate of the air being studied is 0.5 l/min. The absorbing solution is stable for one day. The sensitivity of the method is 0.5 μg in the volume determined. Ketones interfere with determination.

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